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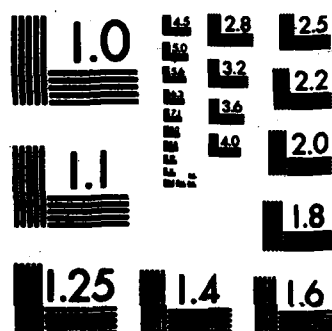
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TDPAC Study of Liquid and Amorphous $\text{Se}_{1-x}\text{Te}_x$ Alloys

by

D. K. Gaskill, John A. Gardner, K. S. Krane, and R. L. Rasera

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TDPAC STUDY OF LIQUID AND AMORPHOUS- $\text{Se}_{1-x}\text{Te}_x$ ALLOYS*

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A time differential perturbed angular correlation study on several liquid and amorphous splat-quenched $\text{Se}_{1-x}\text{Te}_x$ alloys was performed using dilute ^{111}Cd as the tracer. The liquid spectra exhibits an attenuation factor, λ_{22} , consistent with the motional narrowing approximation. The attenuation factor is proportional to the motional correlation time t_c , multiplied by the average square electric quadrupole frequency, $\langle \nu_Q^2 \rangle$. ν_Q has been characterized in amorphous splat-quenched Se and Te, allowing t_c to be computed for these two liquids from the measured λ_{22} . Spectra in both amorphous Se and Te arise from two distinguishable sites with quadrupole frequencies similar to the sites in compounds of Se or Te with In.

We describe here an application of time differential perturbed angular correlation (TDPAC) to the study of molecular dynamics in liquid Se, Te, and $\text{Se}_{1-x}\text{Te}_x$ alloys. When combined with TDPAC spectra on corresponding amorphous solids, these measurements yield a hyperfine correlation time t_c for the tracer nucleus. t_c is approximately equal to the smallest of the characteristic times of molecular rotation, chalcogenbond-breaking, or tracer diffusion. Some of the data presented here on liquid Se and Se-rich alloys have been described previously.^{1,2}

The radioactive tracer used in this work was ^{111}In whose relevant nuclear characteristics are given in Table 1. This tracer decays by electron

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A time differential perturbed angular correlation study on several liquid and amorphous splat-quenched Se _{1-x} Te _x alloys was performed using dilute ¹¹¹ Cd as the tracer. The liquid spectra exhibits an attenuation factor, χ_{22} , consistent with the motional narrowing approximation. The attenuation factor is proportional to the motional correlation time t_c , multiplied by the average square electric quadrupole frequency, $\langle \omega_Q^2 \rangle$. χ_{22} has been characterized in amorphous splat- quenched Se and Te, allowing t_c to be computed for these two liquids from the measured χ_{22} . Spectra in both amorphous Se and Te arise from two distinguishable		

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→ sites with quadrupole frequencies similar to the sites in compounds of Se
or Te with In. ←



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Parent half-life	2.83 days
Energies of γ - γ cascade	171-245 keV
Nuclear spin sequence	$\frac{7+}{2} - \frac{5+}{2} - \frac{1+}{2}$
Angular correlation coefficients:	
A_{22}	-0.180(2)
A_{04}	+0.002(3)
Intermediate nuclear state:	
half-life	84 nsec
spectroscopic nuclear quadrupole moment	+0.83(13) b

TABLE I. Summary of relevant nuclear characteristics of radioactive probe nuclide $^{111}\text{In} \rightarrow ^{111}\text{Cd}$. All data taken from S. Raman and H. J. Kim, Nucl. Data B6, 39 (1971), except quadrupole moment which is from P. Herzog et al., Z. Phys. A 294, 13 (1980).

capture to an excited state of ^{111}Cd , which then decays to its ground state by emitting two successive γ -rays. The emission directions of these γ -rays are strongly correlated. This correlation is perturbed if the nucleus is subject to an external electric field gradient during the time between the emission of the first and second γ -rays. The TDPAC measurement is intended to determine the time dependence of the perturbation of the angular correlation.

Liquid samples were made by placing approximately 50 mg. of the appropriate alloy into a 3 mm diameter quartz tube, adding a few drops of (commercially-obtained carrier-free) ^{111}In -containing HCl solution, evaporating the water, evacuating and sealing the capsule. Experimental measurements were made after the sample had been homogenized at approximately 900°C for 24 hours. These samples were not allowed to freeze

until the series of measurements was complete. The amorphous samples were made by splat-quenching at 78K and were maintained at that temperature until all runs were complete. The experimental setup for the TDPAC measurements consists of four NaI(Tl) scintillation counters, arranged in fixed positions symmetrically in the horizontal plane about the sample furnace or dewar. Delayed coincidences of the 171-245 keV cascade were detected for interdetector angles $\theta=90^\circ$ and 180° by standard fast-slow coincidence circuits. The resulting four spectra were stored in separate memory banks of a multichannel analyzer computer as a function of the time delay t between the two γ -ray emissions. After data were collected for approximately 24 hours, the ratio,

$$R(t) = \frac{2}{3} \left[\frac{C_1(180^\circ, t) C_4(180^\circ, t)}{C_2(90^\circ, t) C_3(90^\circ, t)} \right]^{1/2} - 1 \quad (1)$$

was computed. Here the $C_i(\theta, t)$, $i=1$ to 4, are the time spectra collected by different detector combinations corrected for random coincidences. Representative $R(t)$ spectra are shown in Figures 1-3 for liquid Se, liquid Te, and two amorphous splats, respectively. $R(t)$ is related to the nuclear anisotropy A_{22} and the "perturbing function" $G_{22}(t)$ by

$$R(t) = \frac{A_{22}G_{22}(t)}{1 - \frac{1}{2} A_{22}G_{22}(t)} \quad (2)$$

In solids, the electric field gradient is independent of time, and $G_{22}(t)$ is given by³

$$G_{22}(t) = S_{20} + \sum_{i=1}^3 S_{2i} \cos(\omega_i t) \exp\left(-\frac{1}{2} \delta^2 \omega_i^2 t^2\right), \quad (3)$$

where ω_i , $i=1$ to 3 for Cd, are functions of the quadrupolar frequency ν_Q and electric field gradient (EFG) anisotropy. δ is a measure of the frequency spread due to variations of the EFG in materials which are not

perfect crystals. The S_{21} , $i=0$ to 3, depend on the average orientation of the EFG principal axes. Frequently nuclei occupy sites with differing EFGs, and if so, the observed $G_{22}(t)$ will be the appropriately weighted sum over all sites.

In liquids, molecular reorientation is normally rapid on the (nsec) time scale of the measurements, and the static assumption described above is not correct. If fluctuations are sufficiently rapid, the interaction can be treated in the motional narrowing approximation which yields the simple result,⁴

$$G_{22}(t) = e^{-\lambda_{22}t} \quad , \quad (4)$$

where for Cd,

$$\lambda_{22} = \frac{63}{250} \pi^2 t_c \langle \nu_Q^2 \rangle \quad (5)$$

Here t_c is the hyperfine field correlation time, and $\langle \nu_Q^2 \rangle$ is the average square quadrupole frequency. The data shown in Figs. 1 and 2 follow the simple exponential decay predicted by the above formula. Significantly more structure is evident for the amorphous samples whose spectra are shown in Fig. 3.

Fig. 4 shows the λ_{22} values obtained by fitting the liquid data to Eq. 4. For liquid Te, λ_{22} could be measured accurately only in the supercooled temperature range where it follows an activated temperature dependence with activation energy 0.56 eV. At lower temperatures, λ_{22} for the Se-rich liquids also follows an activated temperature dependence with a concentration-independent activation energy of 0.36 eV.

In order to compute t_c from λ_{22} , $\langle \nu_Q^2 \rangle$ must be known. To the extent that the average surroundings of the In/Cd tracer atom are the same in the liquid and amorphous solid, ν_Q can be found from the TDPAC

spectrum of the splat-quenched solid by fitting to Eq. 3. TDPAC spectra have been measured only on pure amorphous Se and Te. In each case, single-site fits were not adequate, but a two-site fit provided reasonably good agreement with experiment. For amorphous Se, approximately 70% of the tracer atoms are found to have quadrupolar frequency $\nu_Q = 110$ MHz and 30% have $\nu_Q = 70$ MHz. For amorphous Te, approximately 70% have $\nu_Q = 130$ MHz and 30% have $\nu_Q = 70$ MHz. δ is of order 15% for all sites. This result indicates that in the two amorphous solids, In can occupy sites with two different near-neighbor configurations. The quadrupolar frequencies of the two sites in amorphous Se and Te are approximately the same as the frequencies of the two sites in In_2Se_3 and In_2Te_3 respectively.^{5,6}

With these results, $\langle \nu_Q^2 \rangle^{1/2} = 100$ MHz for amorphous Se, and 115 MHz for Te. If $\langle \nu_Q^2 \rangle^{1/2}$ is the same in the liquid, the correlation times for liquid Te and liquid Se at low temperature are given by

$$t_c^{-1} = \nu_0 \exp(-E/kT), \quad (6)$$

where $\nu_0 = 8 \times 10^{11} \text{ sec}^{-1}$ for Se, $2 \times 10^{15} \text{ sec}^{-1}$ for Te, and $E = 0.36 \text{ eV}$ for Se, 0.56 eV for Te. For Se, we have previously conjectured² that the low temperature t_c is the Cd tracer diffusion time. The prefactor for Se is consistent with this suggestion, since ν_0 is the correct order of magnitude for a lattice vibration frequency. For liquid Te, t_c clearly cannot be the tracer diffusion time, since ν_0 is much larger than typical lattice vibration frequencies. It is presently not clear whether t_c in Te or in high-temperature Se is associated with chalcogen bond-breaking. We hope that additional measurements on amorphous solids and Te-rich liquid alloys may help to resolve these questions.

REFERENCES

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- 1) R. L. Rasera and J. Gardner, Phys. Rev. B18 (1978) 6856.
- 2) D. K. Gaskill, J. A. Gardner, K. S. Krane, K. Krusch, and R. L. Rasera, in: Nuclear and Electron Resonance Spectroscopies Applied to Materials Science, eds. E. N. Kaufmann and G. K. Shenoy (North-Holland, Amsterdam, 1981) pp. 369-373.
- 3) H. Frauenfelder and R. M. Steffen, in: Alpha- Beta- and Gamma-Ray Spectroscopy, ed. Siegbahn (North-Holland, Amsterdam, 1965) Chap. 14, A.
- 4) A. Abragam and R. V. Pound, Phys. Rev. 92 (1953) 943.
- 5) K. Krusch and J. A. Gardner, Phys. Rev. B24 (1981) 4587.
- 6) D. K. Gaskill, to be published.

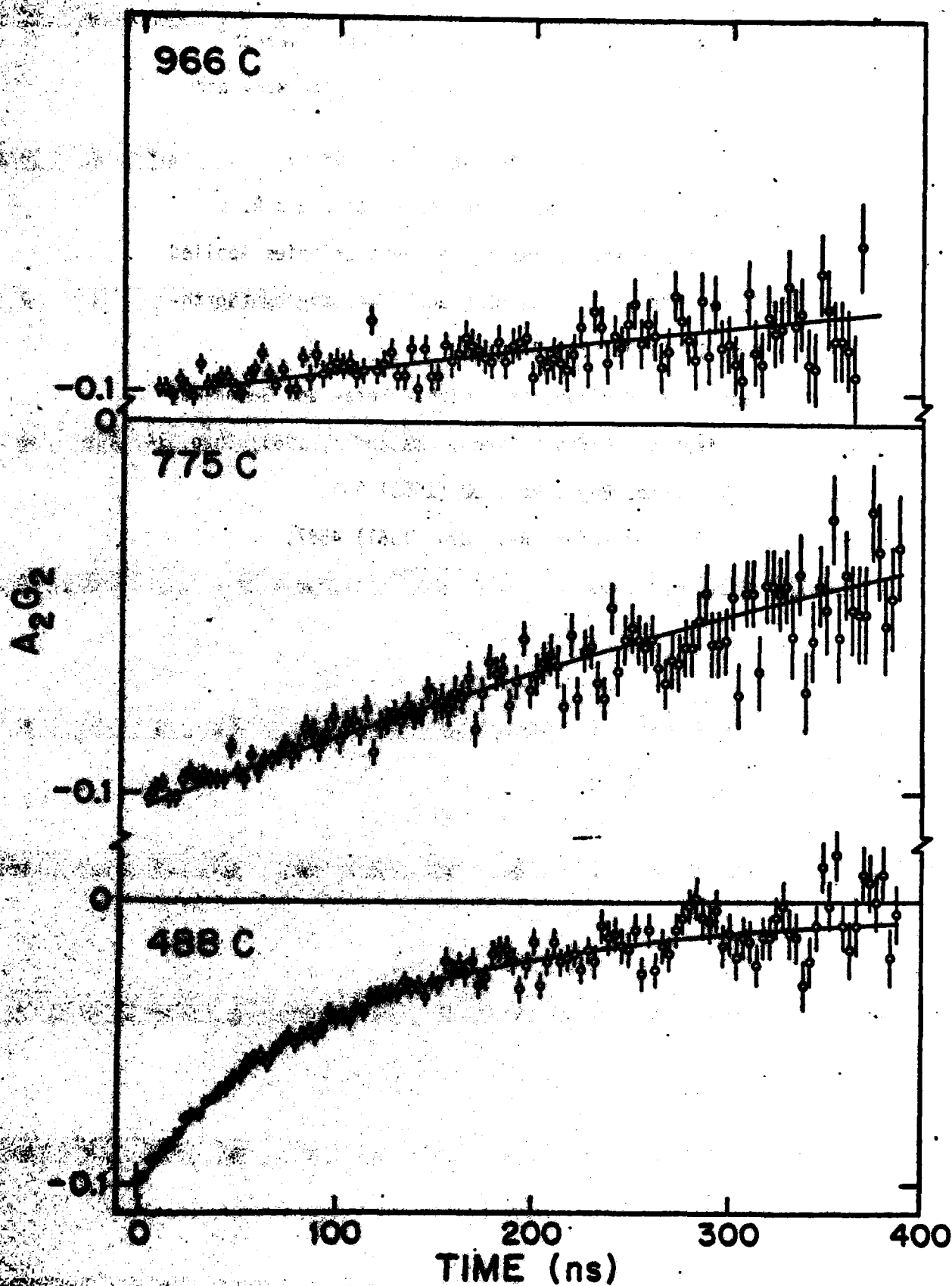


Figure 1. $R(t)$ vs. time for ^{111}Cd in $^{111}\text{Cd Se}$ at three temperatures. The solid lines are best fits to Eq. (1).

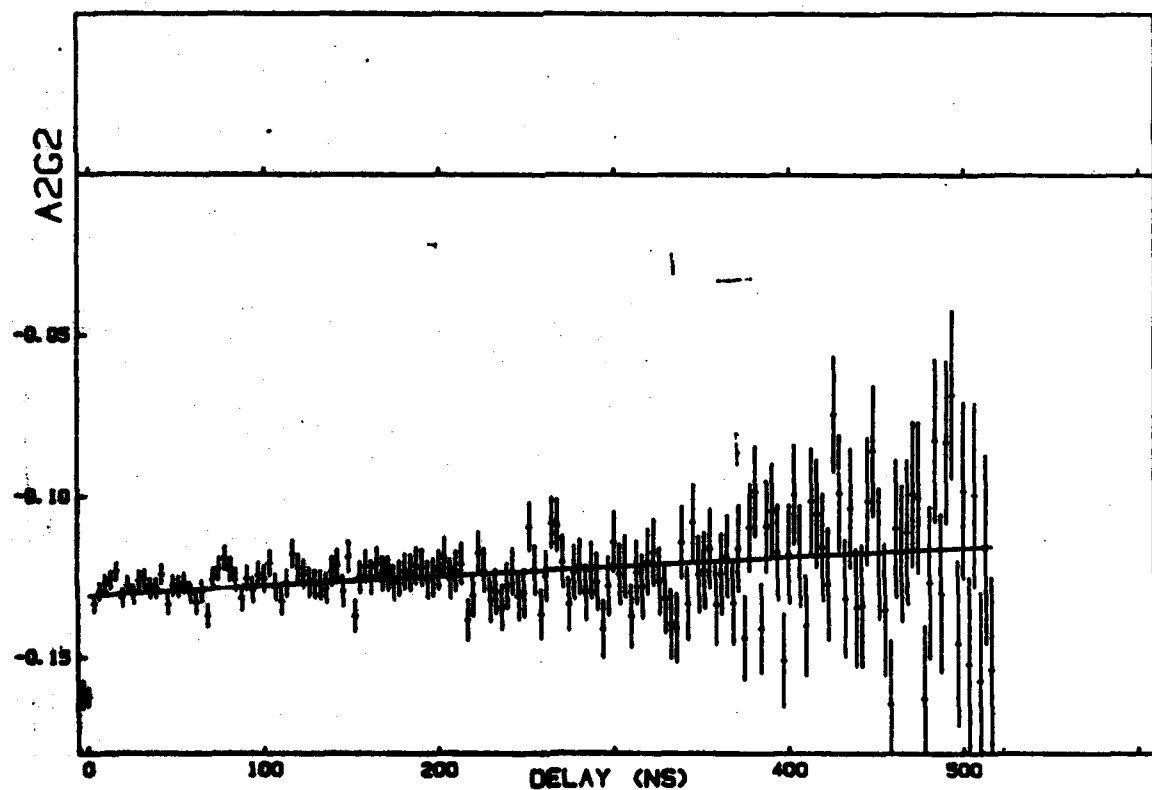
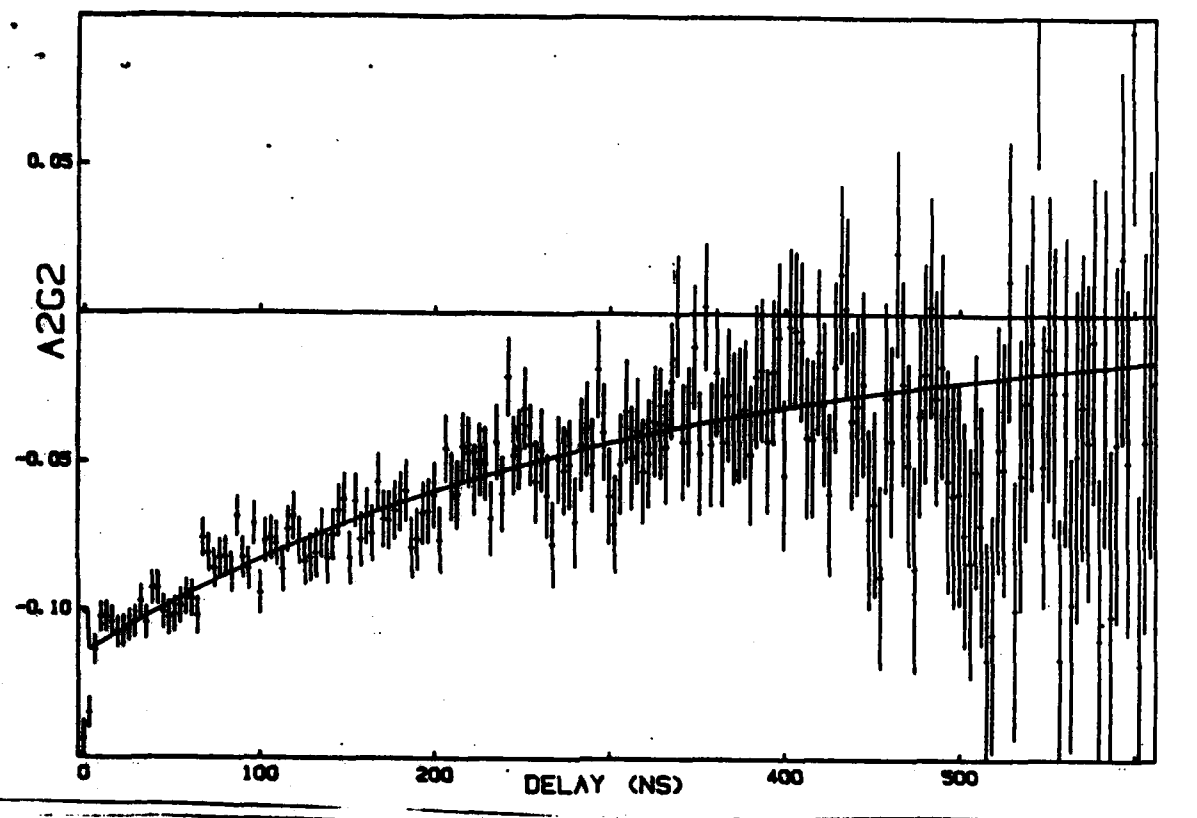


Figure 2. $R(t)$ vs. time for ^{111}Cd in supercooled liquid Te at 269°C (top) and 416°C (bottom). The solid lines are best fits to Equation 4.

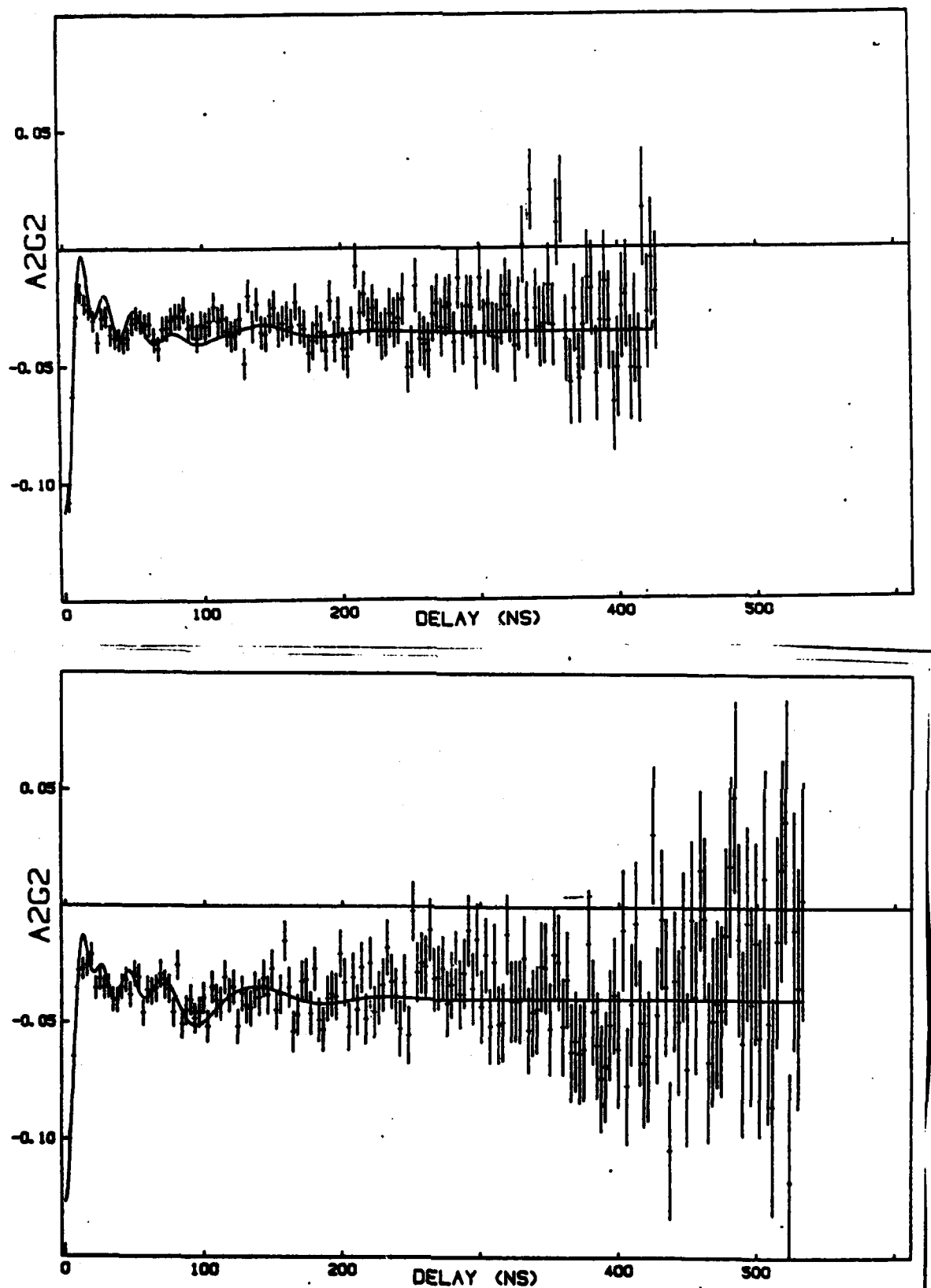


Figure 3. $R(t)$ vs. time for ^{111}Cd in amorphous sput-quenched Se (top) and Te (bottom) at 78 K. The solid lines are best fits to Equation 3.

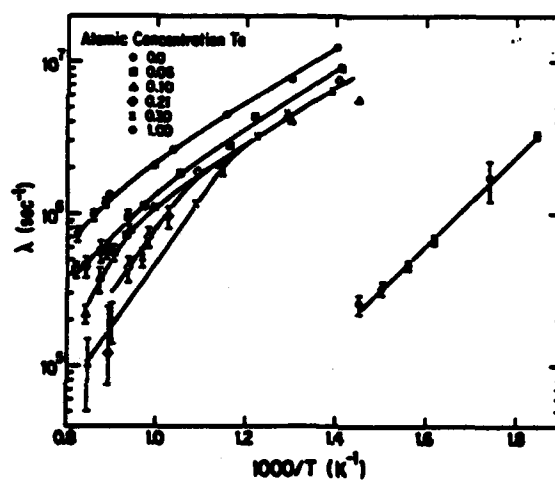


Figure 4. λ_{22} vs. inverse temperature for ^{111}Cd in liquid $\text{Se}_{1-x}\text{Te}_x$ alloys.

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